

# PATENT ABSTRACTS OF JAPAN

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(71)Applicant : MATSUSHITA ELECTRIC IND CO LTD

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(72)Inventor : IWAMOTO KAZUYA  
AOTANI NOBORU  
TAKADA KAZUNORI  
KONDO SHIGEO

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(54) FUEL-SOLID LITHIUM SECONDARY BATTERY

(57)Abstract:

PURPOSE: To provide a full-solid lithium secondary battery having a high service rate of its active material by having positive and negative electrodes and a solid electrolyte, and using a mixture of active material powders and solid electrolyte powders of specified average diameters and mixing ratio as the electrodes.

CONSTITUTION: This full-solid lithium secondary battery has positive and negative electrodes and a solid electrolyte, and at least either one of the electrodes uses a mixture obtained by mixing active material powders of 0.1 to 50 $\mu$ m average diameter with solid electrolyte powders of 0.1 to 50 $\mu$ m average diameter in a weight ratio of 3.0:7.0-9.5-0.5. An amorphous lithium-ion-conductive solid electrolyte (Li<sub>3</sub>PO<sub>4</sub>-Li<sub>2</sub>S-SiS<sub>2</sub> glass and the like) composed chiefly of a sulfide showing a high lithium ion conductivity is used as the solid electrolyte powders. Cobalt acid lithium which shows a high ion conductivity and noble electrode potential is used as the electrode active material powders. Thus the full-solid lithium secondary battery whose electrodes have lowered impedance is obtained.

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**CLAIMS**

[Claim(s)]

[Claim 1]Have an anode, a negative electrode, and a solid electrolyte and at least one electrode, A totally-solid lithium secondary battery using as an electrode a mixture which blends active material powder whose mean particle diameter is 0.1-50 micrometers, and solid electrolyte powder whose mean particle diameter is 0.1-50 micrometers by a weight ratio 3.0:7.0 to 9.5:0.5.

[Claim 2]The totally-solid lithium secondary battery according to claim 1 which is an amorphous lithium-ion-conductivity solid electrolyte in which solid electrolyte powder becomes considering a sulfide as a subject.

[Claim 3]Have an anode, a negative electrode, and a solid electrolyte and at least one electrode mixes an amorphous lithium-ion-conductivity solid electrolyte which becomes considering cobalt acid lithium and a sulfide as a subject, A totally-solid lithium secondary battery in which a solid electrolyte layer is characterized by mean particle diameter of cobalt acid lithium being 5-50 micrometers in a totally-solid lithium secondary battery which is an amorphous lithium-ion-conductivity solid electrolyte which becomes considering a sulfide as a subject.

[Claim 4]The totally-solid lithium secondary battery according to claim 3 whose mean particle diameter of a solid electrolyte in an electrode to mix is 0.1-50 micrometers.

[Claim 5]The totally-solid lithium secondary battery according to claim 3 whose compounding ratio of cobalt acid lithium and a solid electrolyte is 4.0:6.0 to 9.5:0.5 in a weight ratio.

[Claim 6]Have an anode, a negative electrode, and a solid electrolyte and at least one electrode mixes an amorphous lithium-ion-conductivity solid electrolyte which becomes considering cobalt acid lithium and a sulfide as a subject, In a totally-solid lithium secondary battery which is an amorphous lithium-ion-conductivity solid electrolyte in which a solid electrolyte layer becomes considering a sulfide as a subject, A totally-solid lithium secondary battery which cobalt acid lithium is compounded considering a cobalt oxide and a lithium compound as a charge of a start material, and is characterized by the mixture ratio of said cobalt oxide and a lithium compound being Co/Li<1.0 in a weight ratio.

[Claim 7]The totally-solid lithium secondary battery according to claim 6 whose mixture ratio of a cobalt oxide and a lithium compound is Co/Li<0.975 in a weight ratio.

[Claim 8]The totally-solid lithium secondary battery according to claim 6 whose cobalt oxide is  $\text{Co}_3\text{O}_4$ .

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**DETAILED DESCRIPTION**

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[Detailed Description of the Invention]

[0001]

[Industrial Application]This invention relates to the totally-solid lithium secondary battery which used the lithium-ion-conductivity solid electrolyte as an electrolyte.

[0002]

[Description of the Prior Art]In recent years, while a miniaturization and weight saving of portable devices, such as a camcorder/movie and a cellular phone, progress, high-energy-density-ization is desired to the cell as the power supply. Since especially a lithium cell is a substance with an atomic weight with small lithium in which ionization energy is big, research is done briskly [ every direction ] as a cell which can obtain high energy density.

[0003]In the lithium secondary battery used for these uses on the other hand, since the solvent of the organic system is used as an electrolysis solution, it has technical problems, such as a liquid spill and ignition. Therefore, in order to secure the safety of a cell, development of all the solid lithium cells which used the solid electrolyte which comprises a noncombustible solid is desired.

[0004]The method of using the vacuum evaporation techniques, such as a sputtering technique, and thin-film-izing a thin film serves as a subject, and development of all the solid lithium cells is furthered, in order to compensate the lowness of the ion conductivity of the solid electrolyte used. It not only thin-film-izes only a solid electrolyte layer, but by the method of vapor-depositing a thin film, thin film forming also of the electrode material is carried out by vacuum evaporation.

[0005]

[Problem(s) to be Solved by the Invention]However, large-area-izing and high-capacity-izing are difficult for all the solid lithium cells by the method of vapor-depositing a thin film, and a charge and discharge current is as small as several 10-200microA cm<sup>2</sup>, and technical problems, like a manufacturing cost also becomes high occur.

[0006]When powder molding constitutes an electrode to it, large-area-izing and high capacity-ization are attained and it becomes what also has a low manufacturing cost, but it is necessary to mix solid electrolyte powder to electrode active material powder for the following reason.

[0007]In an electrode, electronic transfer is performed during the operation of a cell between the ion and electrode which move in the inside of an electrolyte. Therefore, the electrode of a cell needs to combine ion conductivity and electron conductivity. Generally, when the conductivity of the ion in the inside of an electrode active material and an electrolyte is compared, ion-conductive one in the inside of an electrolyte is high, as a result, electron transfer in the inside of an electrode is performed within an electrode active material or a conducting material, and movement of ion is performed mainly within an electrolyte.

[0008]That is, in the case of the cell using a liquid electrolyte, the electrode created by carrying out application-of-pressure molding of the powdered active material is immersed in an electrolyte, and the electrolyte which permeated in the hole of this powder compact serves as a place of the ion conduction within an electrode.

[0009]On the other hand, since an electrolyte does not permeate in the hole in an electrode in the case of the electrode using the solid electrolyte as an electrolyte, in order to make high ion conductivity in the inside of an electrode, it is necessary [ it ] in an electrode to mix a solid electrolyte. However, since electron transfer is performed, active material particles need to be connected electronically, and when the amount of solid electrolytes in an electrode is superfluous, there is a possibility that this connection may be lost.

[0010]Thus, in a totally-solid battery, an ion conduction course is spoiled depending on the mixture ratio of the solid electrolyte and active material in an electrode, or an electronic conduction course is checked. For this reason, it had a technical problem which the impedance of an electrode becomes high, and the charge and

discharge in a high current become difficult, and becomes what has a low active material utilization factor.

[0011]When the electrolyte was mixed in the electrode, since the active material content in an electrode will become small, it had a technical problem used as what has the low capacity of a cell.

[0012]This invention solves the above technical problem and an object of this invention is to provide the totally-solid lithium secondary battery with a high active material utilization factor using the electrode by powder molding method.

[0013]

[Means for Solving the Problem]As an electrode of a totally-solid lithium secondary battery, a mixture which blends active material powder whose mean particle diameter is 0.1–50 micrometers, and solid electrolyte powder whose mean particle diameter is 0.1–50 micrometers by a weight ratio 3.0:7.0 to 9.5:0.5 is used. An amorphous lithium-ion-conductivity solid electrolyte which becomes considering a sulfide as a subject is used as solid electrolyte powder.

[0014]At least one electrode is a thing containing an amorphous lithium-ion-conductivity solid electrolyte which becomes considering cobalt acid lithium and a sulfide as a subject, In a totally-solid lithium secondary battery which is an amorphous lithium-ion-conductivity solid electrolyte which becomes considering a sulfide as a subject, a solid electrolyte layer uses that whose mean particle diameter of cobalt acid lithium is 5–50 micrometers. That whose mean particle diameter is 0.1 micrometer – 50 micrometers is used as a solid electrolyte contained in an electrode. A ratio of cobalt acid lithium contained in an electrode to a solid electrolyte is set to 4.0:6.0 to 9.5:0.5 by a weight ratio.

[0015]Cobalt acid lithium is compounded considering a cobalt oxide and a lithium compound as a charge of a start material, and sets preferably to  $\text{Co/Li} < 0.975$  the mixture ratio of a cobalt oxide and a lithium compound which are starting materials by a weight ratio at  $\text{Co/Li} < 1.0$  and a pan.  $\text{Co}_3\text{O}_4$  is used as a cobalt oxide.

[0016]

[Function]The solid electrolyte powder whose mean particle diameter is 0.1–50 micrometers, and the active material powder whose mean particle diameter is 0.1–50 micrometers are used, By carrying out pressing of the mixture which blends these powder by a weight ratio 3.0:7.0 to 9.5:0.5, and forming an electrode, Collecting efficiency is raised and it becomes an electrode in which high current charge and discharge are possible at the same time the both sides of the ion conduction course in an electrode and an electronic conduction course can secure and it raises the capacity factor of the active material in an electrode.

[0017]It is required to use the solid electrolyte in which ionic conductivity high in order to improve the ion conductivity within an electrode is shown as a solid electrolyte used for the electrode of such a totally-solid lithium secondary battery. For this reason, especially the thing for which the amorphous lithium-ion-conductivity solid electrolyte which becomes considering the sulfide in which high lithium ion conductivity is shown as a subject is used as solid electrolyte powder is preferred.

[0018]In an electronic-lithium ion mixing conductor, the totally-solid lithium secondary battery which has an energy density possible [ the operation by a high current ] and high can consist of using the cobalt acid lithium in which high ion conductivity and \*\*\*\* electrode potential are shown as an electrode active material. For this reason, especially the thing for which the electrode containing the amorphous lithium-ion-conductivity solid electrolyte which becomes considering cobalt acid lithium and a sulfide as a subject at least is used as an electrode of a totally-solid lithium secondary battery is preferred.

[0019]It is preferred to raise an active material utilization factor using what has a grain boundary few as cobalt acid lithium used as the hindrance of lithium ion conduction. Therefore, when an electrode is constituted by the application-of-pressure molding method, it is preferred to use [ rather than ] what has big particle diameter using the cobalt acid lithium with small particle diameter in which many grain boundaries will exist, and it is preferred that mean particle diameter uses what is 5–50 micrometers as said cobalt acid lithium.

[0020]In the electrode containing the above-mentioned cobalt acid lithium and an amorphous lithium-ion-conductivity solid electrolyte, Collecting efficiency is raised and it becomes an electrode in which high current charge and discharge are possible at the same time the both sides of the ion conduction course in an electrode and an electronic conduction course can secure because the mean particle diameter of the solid electrolyte contained in an electrode shall be 0.1–50 micrometers, and it raises the capacity factor of the active material in an electrode.

[0021]The both sides of the ion conduction course in an electrode and an electronic conduction course are securable by blending cobalt acid lithium and the solid electrolyte which are contained in an electrode in 4.0:6.0 to

9.5:0.5 by a weight ratio. However, in the range with high content of cobalt acid lithium, the active material content in an electrode is high. Since it becomes what has high capacity density, as a ratio of the cobalt acid lithium contained in an electrode to a solid electrolyte, the range of 6.0:4.0 to 9.5:0.5 is especially used preferably by a weight ratio among the above-mentioned mixture ratio.

[0022] Although cobalt acid lithium is compounded considering a cobalt oxide and a lithium compound as a charge of a start material, the particle diameter of the cobalt acid lithium obtained with the mixture ratio at the time of composition changes. The thing using the starting material in which the mixture ratio of a cobalt oxide and a lithium compound turns into a ratio of  $\text{Co/Li} < 1.0$  since only what has mean particle diameter comparatively small in  $\text{Co/Li} \geq 1.0$  is obtained is used preferably. Since cobalt acid lithium with a particle diameter of not less than 5 micrometers can be easily obtained by furthermore being referred to as  $\text{Co/Li} < 0.975$ , as the mixture ratio of the lithium compound and cobalt oxide which are charges of a start material, the range of  $\text{Co/Li} < 0.975$  is used especially preferably.

[0023] Cobalt acid lithium has a crystal structure similar to the cobalt oxide expressed with  $\text{Co}_3\text{O}_4$ , and the particle size of cobalt acid lithium reflects the particle size of  $\text{Co}_3\text{O}_4$  of a starting material well. For this reason, since the particle diameter of the cobalt acid lithium compounded by choosing the particle diameter of  $\text{Co}_3\text{O}_4$  is easily controllable, as a cobalt oxide of a starting material,  $\text{Co}_3\text{O}_4$  is used especially preferably.

[0024]

[Example] Hereafter, although this invention was explained in detail using the example, all operations in these examples were performed all over the dry box which filled inactive gas.

[0025] (Example 1) Details are shown below about the totally-solid lithium secondary battery used  $\text{Li}_3\text{PO}_4$ - $\text{Li}_2\text{S}$ - $\text{SiS}_2$  glass as a solid electrolyte, used titanium disulfide ( $\text{TiS}_2$ ) as positive active material, and using metal lithium foil as a negative electrode.

[0026] First, titanium disulfide is ground so that mean particle diameter may be set to 0.1 micrometer. Subsequently,  $0.01\text{Li}_3\text{PO}_4$ - $0.63\text{Li}_2\text{S}$ - $0.36\text{SiS}_2$  glass is ground, and it classifies so that mean particle diameter may be set to 0.1, 25 and 50, and 75 or 100 micrometers. Weighing of disulfide titanium powder and each  $0.01\text{Li}_3\text{PO}_4$ - $0.63\text{Li}_2\text{S}$ - $0.36\text{SiS}_2$  glass powder which classified is carried out so that it may be set to 1:9-10:0 by a weight ratio, it is mixed enough, and it is considered as anode powder. Weighing of the quantity which contains the titanium disulfide of fixed theoretical capacity for this anode powder was carried out, pressing was carried out to 10 mmphi, and it was considered as the anode.

[0027] Pressing of the  $0.01\text{Li}_3\text{PO}_4$ - $0.63\text{Li}_2\text{S}$ - $0.36\text{SiS}_2$  glass powder is carried out. It was considered as the solid electrolyte layer with 0.5 mm [ in thickness ], and a diameter [ phi ] of 10 mm, after facing across and welding this solid electrolyte layer by pressure with the metal lithium foil which is the above-mentioned anode and a negative electrode, it inserted in the cell case, and it was considered as the totally-solid lithium secondary battery.

[0028] This totally-solid lithium secondary battery is discharged to 1.8V according to the constant current of 500microA, and the result of having investigated the titanium disulfide capacity factor which is positive active material is shown in drawing 1.

[0029] The result at the time of using that whose mean particle diameter of 1, 2, 3, 4, 5, and \*\*\*\*\*  $0.01\text{Li}_3\text{PO}_4$ - $0.63\text{Li}_2\text{S}$ - $0.36\text{SiS}_2$  glass powder is 0.1 micrometer, 25 micrometers, 50 micrometers, 75 micrometers, and 100 micrometers is shown among a figure.

[0030] When the mean particle diameter of titanium disulfide is 0.1 micrometer from this result, When the mean particle diameter of  $0.01\text{Li}_3\text{PO}_4$ - $0.63\text{Li}_2\text{S}$ - $0.36\text{SiS}_2$  glass powder is 50 micrometers or less, 0. Titanium disulfide and  $0.01\text{Li}_3\text{PO}_4$ - $0.63\text{Li}_2\text{S}$ - $0.36\text{SiS}_2$  glass. The powdered rate showed the high capacity factor in 3.0:7.0 to 7.0:3.0 by the weight ratio, and the capacity factor of 78% was acquired at the maximum.

[0031] (Example 2) Except the mean particle diameter of titanium disulfide having been 25 micrometers, the same totally-solid lithium secondary battery as Example 1 was constituted, and the same examination was done.

[0032] The result is shown in drawing 2. 6, 7, 8, 9, and 10 show among a figure the result at the time of using that whose mean particle diameter of  $0.01\text{Li}_3\text{PO}_4$ - $0.63\text{Li}_2\text{S}$ - $0.36\text{SiS}_2$  glass powder is 0.1 micrometer, 25 micrometers, 50 micrometers, 75 micrometers, and 100 micrometers respectively.

[0033] When the mean particle diameter of titanium disulfide is 25 micrometers from this result, 0. When the mean

particle diameter of  $0.01\text{Li}_3\text{PO}_4-0.63\text{Li}_2\text{S}-0.36\text{SiS}_2$  glass powder is 50 micrometers or less, the rate of titanium disulfide and  $0.01\text{Li}_3\text{PO}_4-0.63\text{Li}_2\text{S}-0.36\text{SiS}_2$  glass powder. The weight ratio showed the high capacity factor in 3.0:7.0 to 7.0:3.0, and the capacity factor of 76% was acquired at the maximum.

[0034](Example 3) Except the mean particle diameter of titanium disulfide having been 50 micrometers, the same totally-solid lithium secondary battery as Example 1 was constituted, and the same examination was done.

[0035]The result is shown in drawing 3. 11, 12, 13, 14, and 15 show among a figure the result at the time of using that whose mean particle diameter of  $0.01\text{Li}_3\text{PO}_4-0.63\text{Li}_2\text{S}-0.36\text{SiS}_2$  glass powder is 0.1 micrometer, 25

micrometers, 50 micrometers, 75 micrometers, and 100 micrometers respectively.

[0036]When the mean particle diameter of titanium disulfide is 50 micrometers from this result, 0. When the mean particle diameter of  $0.01\text{Li}_3\text{PO}_4-0.63\text{Li}_2\text{S}-0.36\text{SiS}_2$  glass powder is 50 micrometers or less, the rate of titanium disulfide and  $0.01\text{Li}_3\text{PO}_4-0.63\text{Li}_2\text{S}-0.36\text{SiS}_2$  glass powder. The weight ratio showed the high capacity factor in 3.0:7.0 to 7.0:3.0, and the capacity factor of 75% was acquired at the maximum.

[0037](Comparative example 1) Except the mean particle diameter of titanium disulfide having been 75 micrometers, the same totally-solid lithium secondary battery as Example 1 was constituted, and the same examination was done.

[0038]The result is shown in drawing 4. 16, 17, 18, 19, and 20 show among a figure the result at the time of using that whose mean particle diameter of  $0.01\text{Li}_3\text{PO}_4-0.63\text{Li}_2\text{S}-0.36\text{SiS}_2$  glass powder is 0.1 micrometer, 25

micrometers, 50 micrometers, 75 micrometers, and 100 micrometers respectively.

[0039]When the mean particle diameter of titanium disulfide is 75 micrometers from this result, The rate of titanium disulfide and  $0.01\text{Li}_3\text{PO}_4-0.63\text{Li}_2\text{S}-0.36\text{SiS}_2$  glass powder was only a capacity factor of 45% at the maximum, although the peak of the capacity factor of titanium disulfide was accepted focusing on 5.0:5.0 by the weight ratio.

[0040](Comparative example 2) Except the mean particle diameter of titanium disulfide having been 100 micrometers, the same totally-solid lithium secondary battery as Example 1 was constituted, and the same examination was done.

[0041]The result is shown in drawing 5. 21, 22, 23, 24, and 25 show among a figure the result at the time of using that whose mean particle diameter of  $0.01\text{Li}_3\text{PO}_4-0.63\text{Li}_2\text{S}-0.36\text{SiS}_2$  glass powder is 0.1 micrometer, 25

micrometers, 50 micrometers, 75 micrometers, and 100 micrometers respectively.

[0042]When the mean particle diameter of titanium disulfide is 100 micrometers from this result, The rate of titanium disulfide and  $0.01\text{Li}_3\text{PO}_4-0.63\text{Li}_2\text{S}-0.36\text{SiS}_2$  glass powder was only a capacity factor of 33% at the maximum, although the peak of the capacity factor of titanium disulfide was accepted focusing on 5.0:5.0 by the weight ratio.

[0043]From the above result, the mean particle diameter of the  $0.01\text{Li}_3\text{PO}_4-0.63\text{Li}_2\text{S}-0.36\text{SiS}_2$  glass powder which is a solid electrolyte 0.1-50 micrometers, Using what is 0.1-50 micrometers, by a weight ratio, the mean particle diameter of the disulfide titanium powder which is positive active material blends these powder, and it 3.0:7.0 to 7.0:3.0 mixing and by carrying out pressing and forming an electrode, It turned out that the both sides of the ion conduction course in an electrode and an electronic conduction course can secure, and the capacity factor of the titanium disulfide which is the positive active material in an electrode is raised.

[0044](Example 4) Details are shown below about the totally-solid lithium secondary battery used  $\text{Li}_3\text{PO}_4-\text{Li}_2\text{S}-\text{SiS}_2$  glass as a solid electrolyte, used graphite as positive active material, and using metal lithium foil as a negative electrode.

[0045]First, graphite is ground so that mean particle diameter may be set to 0.1 micrometer. Subsequently,  $0.01\text{Li}_3\text{PO}_4-0.63\text{Li}_2\text{S}-0.36\text{SiS}_2$  glass is ground, and it classifies so that mean particle diameter may be set to 0.1 micrometer, 25 micrometers, 50 micrometers, 75 micrometers, and 100 micrometers. Weighing of graphite and each  $0.01\text{Li}_3\text{PO}_4-0.63\text{Li}_2\text{S}-0.36\text{SiS}_2$  glass powder which classified is carried out so that it may be set to 1:9-10:0 by a weight ratio, it is mixed enough, and it is considered as anode powder. Weighing of the quantity which contains the graphite of fixed theoretical capacity for this anode powder was carried out, pressing was carried out to 10 mmphi, and it was considered as the anode.

[0046]Pressing of the  $0.01\text{Li}_3\text{PO}_4-0.63\text{Li}_2\text{S}-0.36\text{SiS}_2$  glass powder is carried out, It was considered as the solid

electrolyte layer with 0.5 mm [ in thickness ], and a diameter [ phi ] of 10 mm, after facing across and welding this solid electrolyte layer by pressure with the metal lithium foil which is the above-mentioned anode and a negative electrode, it inserted in the cell case, and it was considered as the totally-solid lithium secondary battery.

[0047] This totally-solid lithium secondary battery was discharged to 0V according to the constant current of 300microA, and the capacity factor of the graphite which is positive active material was investigated. As a result, when the mean particle diameter of graphite is 0.1 micrometer, 0. When the mean particle diameter of  $0.01\text{Li}_3\text{PO}_4-0.63\text{Li}_2\text{S}-0.36\text{SiS}_2$  glass powder is 50 micrometers or less, the rate of titanium disulfide and  $0.01\text{Li}_3\text{PO}_4-0.63\text{Li}_2\text{S}-0.36\text{SiS}_2$  glass powder. The weight ratio showed the high capacity factor in 3.0:7.0 to 7.0:3.0, and the capacity factor of 75% was acquired at the maximum.

[0048] (Example 5) Except the mean particle diameter of graphite having been 25 micrometers, the same totally-solid lithium secondary battery as Example 4 was constituted, and the same examination was done. As a result, when the mean particle diameter of graphite is 25 micrometers, 0. When the mean particle diameter of  $0.01\text{Li}_3\text{PO}_4-0.63\text{Li}_2\text{S}-0.36\text{SiS}_2$  glass powder is 50 micrometers or less, the rate of graphite and  $0.01\text{Li}_3\text{PO}_4-0.63\text{Li}_2\text{S}-0.36\text{SiS}_2$  glass powder. The weight ratio showed the high capacity factor in 3.0:7.0 to 7.0:3.0, and the capacity factor of 73% was acquired at the maximum.

[0049] (Example 6) Except the mean particle diameter of graphite having been 50 micrometers, the same totally-solid lithium secondary battery as Example 4 was constituted, and the same examination was done. As a result, when the mean particle diameter of graphite is 50 micrometers, 0. When the mean particle diameter of  $0.01\text{Li}_3\text{PO}_4-0.63\text{Li}_2\text{S}-0.36\text{SiS}_2$  glass powder is 50 micrometers or less, the rate of graphite and  $0.01\text{Li}_3\text{PO}_4-0.63\text{Li}_2\text{S}-0.36\text{SiS}_2$  glass powder. The weight ratio showed the high capacity factor in 3.0:7.0 to 7.0:3.0, and the capacity factor of 70% was acquired at the maximum.

[0050] (Comparative example 3) Except the mean particle diameter of graphite having been 75 micrometers, the same totally-solid lithium secondary battery as Example 4 was constituted, and the same examination was done. As a result, when the mean particle diameter of graphite is 75 micrometers, although the peak of the capacity factor of graphite is accepted focusing on 5.0:5.0 by a weight ratio, the rate of graphite and  $0.01\text{Li}_3\text{PO}_4-0.63\text{Li}_2\text{S}-0.36\text{SiS}_2$  glass powder, It was only a capacity factor of 25% at the maximum.

[0051] (Comparative example 4) Except the mean particle diameter of graphite having been 100 micrometers, the same totally-solid lithium secondary battery as Example 4 was constituted, and the same examination was done. As a result, when the mean particle diameter of graphite is 100 micrometers, although the peak of the capacity factor of graphite is accepted focusing on 5.0:5.0 by a weight ratio, the rate of graphite and  $0.01\text{Li}_3\text{PO}_4-0.63\text{Li}_2\text{S}-0.36\text{SiS}_2$  glass powder, It was only a capacity factor of 8% at the maximum.

[0052] From the above result, the mean particle diameter of the  $0.01\text{Li}_3\text{PO}_4-0.63\text{Li}_2\text{S}-0.36\text{SiS}_2$  glass powder which is a solid electrolyte 0.1-50 micrometers, Using what is 0.1-50 micrometers, by a weight ratio, the mean particle diameter of the graphite powder which is positive active material blends these powder, and it 3.0:7.0 to 7.0:3.0 mixing and by carrying out pressing and forming an electrode, It turned out that the both sides of the ion conduction course in an electrode and an electronic conduction course can secure, and the capacity factor of the graphite which is the positive active material in an electrode is raised.

[0053] (Example 7) It is made to be the same as that of Example 1 except having used the nickel acid lithium expressed with  $\text{LiNiO}_2$  as positive active material in this example,  $\text{Li}_3\text{PO}_4-\text{Li}_2\text{S}-\text{SiS}_2$  glass was used as a solid electrolyte, metal lithium foil was used as a negative electrode, and the totally-solid lithium secondary battery was constituted.

[0054] First, nickel acid lithium was compounded by the following methods. Nickel acid lithium mixed lithium hydroxide ( $\text{LiOH}$ ) with nickel oxide ( $\text{NiO}$ ), and compounded it by calcinating at 1000 \*\* among the atmosphere. This compound nickel acid lithium was ground, and it classified so that mean particle diameter might be set to 1 micrometer, 10 micrometers, 50 micrometers, 75 micrometers, and 100 micrometers.

[0055] The  $0.01\text{Li}_3\text{PO}_4-0.63\text{Li}_2\text{S}-0.36\text{SiS}_2$  glass powder obtained by the same method as Example 1 as a solid electrolyte is ground, and it classifies so that mean particle diameter may be set to 1 micrometer. Weighing of nickel acid lithium and  $0.01\text{Li}_3\text{PO}_4-0.63\text{Li}_2\text{S}-0.36\text{SiS}_2$  glass powder which were obtained above is carried out so that it may be set to 1:9-10:0 by a weight ratio, they are mixed enough, and it is considered as anode powder.

Weighing of the quantity which contains nickel acid lithium of fixed theoretical capacity for this anode powder was carried out, pressing was carried out to 10 mmphi, and it was considered as the anode.

[0056]Pressing of the  $0.01\text{Li}_3\text{PO}_4-0.63\text{Li}_2\text{S}-0.36\text{SiS}_2$  glass powder is carried out, It was considered as the solid electrolyte layer with 0.5 mm [ in thickness ], and a diameter [ phi ] of 10 mm, after facing across and welding this solid electrolyte layer by pressure with the metal lithium foil which is the above-mentioned anode and a negative electrode, it inserted in the cell case, and the totally-solid lithium secondary battery was constituted. As negative electrode active material, 100-micrometer-thick metal lithium foil was used.

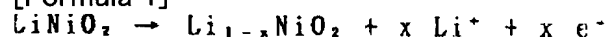
[0057]Thus, the obtained totally-solid lithium secondary battery was charged by the constant current of 100microA, and charging capacity until terminal voltage shows 4.3V was measured.

[0058]The relation between nickel acid lithium in an anode, the rate of  $0.01\text{Li}_3\text{PO}_4-0.63\text{Li}_2\text{S}-0.36\text{SiS}_2$  glass powder, and charging capacity is shown in drawing 6. However, charging capacity is converted into the move electron number (\*\* 1) (inner x value) to nickel acid lithium, and a vertical axis shows it.

[0059]26, 27, 28, 29, and 30 show among a figure the result at the time of using that whose mean particle diameter of nickel acid lithium is 1 micrometer, 10 micrometers, 50 micrometers, 75 micrometers, and 100 micrometers respectively.

[0060]

[Formula 1]



[0061]From this result, when the mean particle diameter of  $0.01\text{Li}_3\text{PO}_4-0.63\text{Li}_2\text{S}-0.36\text{SiS}_2$  glass powder is 1 micrometer, When the mean particle diameter of nickel acid lithium is 50 micrometers or less, the rate of nickel acid lithium and  $0.01\text{Li}_3\text{PO}_4-0.63\text{Li}_2\text{S}-0.36\text{SiS}_2$  glass powder shows high charging capacity in 4.0:6.0 to 9.5:0.5 by a weight ratio, It turned out that a high active material utilization factor can be obtained.

[0062]As mentioned above, according to this invention, it turned out that the totally-solid lithium secondary battery in which a high active material utilization factor is shown is obtained.

[0063](Example 8) It is made to be the same as that of Example 1 except having used the cobalt-acid-lithium powder expressed with  $\text{LiCoO}_2$  as an electrode active material in this example,  $\text{Li}_3\text{PO}_4-\text{Li}_2\text{S}-\text{SiS}_2$  glass was used as a solid electrolyte, metal lithium foil was used as a negative electrode, and the totally-solid lithium secondary battery was constituted.

[0064]First, cobalt acid lithium ( $\text{LiCoO}_2$ ) was compounded by the following methods. Cobalt oxide ( $\text{Co}_3\text{O}_4$ ) and lithium carbonate ( $\text{Li}_2\text{CO}_3$ ) were compounded weighing and by mixing and calcinating at 900 \*\* among the atmosphere so that it might become a ratio of  $\text{Co}/\text{Li}=0.96$ . Thus, it was 8 micrometers when the mean particle diameter of the obtained cobalt acid lithium was measured.

[0065]The  $0.01\text{Li}_3\text{PO}_4-0.63\text{Li}_2\text{S}-0.36\text{SiS}_2$  glass powder obtained by the same method as Example 1 as a solid electrolyte is ground, and it classifies so that mean particle diameter may be set to 0.1 micrometer, 1 micrometer, 10 micrometers, 50 micrometers, and 100 micrometers. Weighing of the cobalt acid lithium obtained above and each  $0.01\text{Li}_3\text{PO}_4-0.63\text{Li}_2\text{S}-0.36\text{SiS}_2$  glass powder which classified is carried out so that it may be set to 1:9-10:0 by a weight ratio, it is mixed enough, and it is considered as anode powder. Weighing of the quantity which contains cobalt acid lithium of fixed theoretical capacity for this anode powder was carried out, pressing was carried out to 10 mmphi, and it was considered as the anode.

[0066]Pressing of the  $0.01\text{Li}_3\text{PO}_4-0.63\text{Li}_2\text{S}-0.36\text{SiS}_2$  glass powder is carried out, It was considered as the solid electrolyte layer with 0.5 mm [ in thickness ], and a diameter [ phi ] of 10 mm, after facing across and welding this solid electrolyte layer by pressure with the metal lithium foil which is the above-mentioned anode and a negative electrode, it inserted in the cell case, and the totally-solid lithium secondary battery was constituted. As negative electrode active material, 100-micrometer-thick metal lithium foil was used.

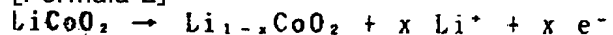
[0067]Thus, the obtained totally-solid lithium secondary battery was charged by the constant current of 200microA, and charging capacity until terminal voltage shows 4.5V was measured.

[0068]The relation between cobalt acid lithium in an anode, the rate of  $0.01\text{Li}_3\text{PO}_4-0.63\text{Li}_2\text{S}-0.36\text{SiS}_2$  glass powder, and charging capacity is shown in drawing 7. However, charging capacity is converted into the move electron number (\*\* 2) (inner x value) to cobalt acid lithium, and a vertical axis shows it.



[0069]

[Formula 2]



[0070]The capacity density of per anode 1g is calculated from the charging capacity produced by doing in this way. The relation between cobalt acid lithium in an anode, the rate of  $0.01\text{Li}_3\text{PO}_4-0.63\text{Li}_2\text{S}-0.36\text{SiS}_2$  glass powder, and the capacity density of per anode 1g is shown in drawing 8.

[0071]The inside [ 36, 37, 38, 39, and 40 ] 31, 32, 33, 34, and 35 of drawing 7 and drawing 8. The result of having used that whose mean particle diameter of  $0.01\text{Li}_3\text{PO}_4-0.63\text{Li}_2\text{S}-0.36\text{SiS}_2$  glass powder is 0.1 micrometer, 1 micrometer, 10 micrometers, 50 micrometers, and 100 micrometers respectively is shown.

[0072]When the particle diameter of cobalt acid lithium is 8 micrometers from the result shown in drawing 7. When the mean particle diameter of  $0.01\text{Li}_3\text{PO}_4-0.63\text{Li}_2\text{S}-0.36\text{SiS}_2$  glass powder is 0.1-50 micrometers, 0. Cobalt acid lithium and  $0.01\text{Li}_3\text{PO}_4-0.63\text{Li}_2\text{S}-0.36\text{SiS}_2$  glass. It turned out that a powdered rate shows high charging capacity in 4.0:6.0 to 9.5:0.5 by a weight ratio, and can obtain a high active material utilization factor. From the result shown in drawing 8. It turned out that the totally-solid lithium secondary battery which the rate of cobalt acid lithium and  $0.01\text{Li}_3\text{PO}_4-0.63\text{Li}_2\text{S}-0.36\text{SiS}_2$  glass powder shows high capacity density especially in 6.0:4.0 to 9.5:0.5 by a weight ratio is obtained.

[0073]As mentioned above, according to this invention, it turned out that the totally-solid lithium secondary battery in which a high active material utilization factor is shown, and high capacity density is shown is obtained.

[0074](Example 9) In this example, it replaces with  $0.01\text{Li}_3\text{PO}_4-0.63\text{Li}_2\text{S}-0.36\text{SiS}_2$  as an electrolyte, 0. Except having used the lithium-ion-conductivity noncrystalline solid electrolyte expressed with  $60\text{Li}_2\text{S}-0.40\text{SiS}_2$ , the totally-solid lithium secondary battery was constituted from the same method as Example 8, and the characteristic was evaluated.

[0075]As a result, the relation of the active material utilization factor and capacity density to the mixture ratio of the active material and solid electrolyte in an electrode was the same as that of Example 8 almost.

[0076]As mentioned above, according to this invention, it turned out that the totally-solid lithium secondary battery in which a high active material utilization factor is shown, and high capacity density is shown is obtained.

[0077](Example 10) In this example, it replaces with  $0.01\text{Li}_3\text{PO}_4-0.63\text{Li}_2\text{S}-0.36\text{SiS}_2$  as an electrolyte, 0. Except having used the lithium-ion-conductivity noncrystalline solid electrolyte expressed with  $04\text{Li}_4\text{SiO}_4-0.58\text{Li}_2\text{S}-0.38\text{SiS}_2$ , all the solid lithium cells were constituted from the same method as Example 8, and the characteristic was evaluated.

[0078]As a result, the relation of the active material utilization factor and capacity density to the mixture ratio of the active material and solid electrolyte in an electrode was the same as that of Example 8 almost.

[0079]As mentioned above, according to this invention, it turned out that the totally-solid lithium secondary battery in which a high active material utilization factor is shown, and high capacity density is shown is obtained.

[0080](Example 11) In this example, it replaces with  $0.01\text{Li}_3\text{PO}_4-0.63\text{Li}_2\text{S}-0.36\text{SiS}_2$  as an electrolyte, 0. Except having used the lithium-ion-conductivity noncrystalline solid electrolyte expressed with  $02\text{Li}_2\text{O}-0.59\text{Li}_2\text{S}-0.39\text{SiS}_2$ , the totally-solid lithium secondary battery was constituted from the same method as Example 8, and the characteristic was evaluated.

[0081]As a result, the relation of the active material utilization factor and capacity density to the mixture ratio of the active material and solid electrolyte in an electrode was the same as that of Example 8 almost.

[0082]As mentioned above, according to this invention, it turned out that the totally-solid lithium secondary battery in which a high active material utilization factor is shown, and high capacity density is shown is obtained.

[0083](Example 12) In this example, it replaces with  $0.01\text{Li}_3\text{PO}_4-0.63\text{Li}_2\text{S}-0.36\text{SiS}_2$  as an electrolyte, 0. Except having used the lithium-ion-conductivity noncrystalline solid electrolyte expressed with  $60\text{Li}_2\text{S}-0.35\text{SiS}_2-0.05\text{P}_2\text{S}_5$ , the totally-solid lithium secondary battery was constituted from the same method as Example 8, and the characteristic was evaluated.

[0084]As a result, the relation of the active material utilization factor and capacity density to the mixture ratio of the active material and solid electrolyte in an electrode was the same as that of Example 8 almost.

[0085]As mentioned above, according to this invention, it turned out that the totally-solid lithium secondary battery in which a high active material utilization factor is shown, and high capacity density is shown is obtained. [0086](Example 13) In order to investigate a relation with the mixture ratio of the active material and solid electrolyte in the active material powder grain size at the time of using cobalt acid lithium as an electrode active material, and an electrode in this example, The totally-solid lithium secondary battery was constituted like Example 8 using the cobalt-acid-lithium powder of various particle diameter as an electrode active material, and the characteristic was evaluated.

[0087]It compounded by calcinating cobalt oxide and lithium carbonate at 900 \*\* among the atmosphere as cobalt acid lithium ( $\text{LiCoO}_2$ ), using weighing and the mixed thing as a starting material so that it may become a ratio of  $\text{Co/Li}=0.92$ . Thus, grinding classification of the obtained cobalt acid lithium is carried out, and it classifies so that mean particle diameter may be set to 0.1 micrometer, 1 micrometer, 5 micrometers, 10 micrometers, 50 micrometers, and 100 micrometers.

[0088]As a solid electrolyte, the  $0.01\text{Li}_3\text{PO}_4-0.63\text{Li}_2\text{S}-0.36\text{SiS}_2$  glass powder obtained by the same method as Example 1 was ground, and what was classified so that mean particle diameter might be set to 1 micrometer was used.

[0089]The totally-solid lithium secondary battery obtained by creating like Example 8 using these was charged by the same method as Example 8, and the charging capacity was measured.

[0090]The relation between nickel acid lithium in the anode of cobalt acid lithium of each mean particle diameter, the rate of  $0.01\text{Li}_3\text{PO}_4-0.63\text{Li}_2\text{S}-0.36\text{SiS}_2$  glass powder, and charging capacity is shown in drawing 9.

[0091]41, 42, 43, 44, 45, and 46 show among a figure the result at the time of using that whose mean particle diameter of cobalt acid lithium is 0.1 micrometer, 1 micrometer, 5 micrometers, 10 micrometers, 50 micrometers, and 100 micrometers respectively.

[0092]From this result. When the mean particle diameter of cobalt acid lithium is 5-50 micrometers, the rate of cobalt acid lithium and  $0.01\text{Li}_3\text{PO}_4-0.63\text{Li}_2\text{S}-0.36\text{SiS}_2$  glass powder shows high charging capacity in 4.0:6.0 to 9.5:0.5 by a weight ratio. It turned out that a high active material utilization factor can be obtained.

[0093]As mentioned above, according to this invention which sets mean particle diameter of cobalt acid lithium to 5-50 micrometers, it turned out that the totally-solid lithium secondary battery in which a high active material utilization factor is shown is obtained.

[0094](Example 14) In this example, using the cobalt acid lithium which compounded cobalt oxide of the various mixture ratio, and the mixture of lithium carbonate as a starting material as an electrode active material, the totally-solid lithium secondary battery was constituted and the characteristic was evaluated.

[0095]It compounded by calcinating cobalt oxide and lithium carbonate at 900 \*\* among the atmosphere as cobalt acid lithium ( $\text{LiCoO}_2$ ), using weighing and the mixed thing as a starting material so that it may become a ratio of  $\text{Co/Li}=0.90 - 1.05$  as shown in (Table 1).

[0096]Thus, the result of having measured the mean particle diameter of the obtained cobalt acid lithium is shown in (Table 1). Inside "lump" is not powdered and it is shown that massive cobalt acid lithium was obtained (Table 1).

[0097]

[Table 1]

Co/Li	0.90	0.925	0.95	0.975	1.00	1.025	1.05
平均粒径	塊	塊	8	6	4	3	3

[0098]Thus, the totally-solid lithium secondary battery consisted of the following methods using the obtained cobalt acid lithium.

[0099]About the thing of  $\text{Co/Li}=0.90$  and 0.925, the obtained sample was ground among the above-mentioned cobalt acid lithium, and what was classified so that mean particle diameter might be set to 8 micrometers was used as an electrode active material. About the thing ( $\text{Co/Li}>0.925$ ) of other presentations, the sample after calcination was used as an electrode active material as it was.

[0100]As a solid electrolyte, the  $0.01\text{Li}_3\text{PO}_4-0.63\text{Li}_2\text{S}-0.36\text{SiS}_2$  glass powder with a mean particle diameter of 1 micrometer used in Example 13 is used, Weighing of this  $0.01\text{Li}_3\text{PO}_4-0.63\text{Li}_2\text{S}-0.36\text{SiS}_2$  glass powder was carried out so that it might be set to 1:9 by above-mentioned cobalt-acid-lithium powder and weight ratio, it was mixed enough, and it was considered as anode powder. Except having used this positive electrode material, the totally-solid lithium secondary battery was constituted from the same method as Example 8, it charged by the same method as Example 8, and that charging capacity was investigated.

[0101]Thus, cobalt acid lithium in an anode, the rate of  $0.01\text{Li}_3\text{PO}_4-0.63\text{Li}_2\text{S}-0.36\text{SiS}_2$  glass powder, and the relation of charging capacity are shown in drawing 10 about cobalt acid lithium of each obtained mean particle diameter.

[0102]The inside of a figure, and 47, 48, 49, 50, 51, 52 and 53, It is the result of using the cobalt acid lithium which compounded as a starting material what mixed lithium carbonate with cobalt oxide respectively by the ratio of  $\text{Co}/\text{Li}=0.90, 0.925, 0.95, \text{ and } 0.975, 1.00, 1.025 \text{ and } 1.05$ .

[0103]The active material utilization factor in which cobalt acid lithium mixed by the ratio of  $\text{Co}/\text{Li}<1.0$  and the cobalt acid lithium which compounded lithium carbonate as a starting material are more expensive than this result is shown, It turned out that a high active material utilization factor is especially shown by using the starting material mixed by the ratio of  $\text{Co}/\text{Li}<0.975$  furthermore.

[0104]Especially about the thing of  $\text{Co}/\text{Li}=1.00, \text{ and } 1.025 \text{ and } 1.05$ , it turned out to it that only a low active material utilization factor is shown and it is not suitable for the electrode active material of high capacity density in the range in which the content of cobalt acid lithium exceeds 50wt%.

[0105]By as mentioned above, the thing for which  $\text{Co}/\text{Li}<1.0$  and the mixture mixed so that further especially  $\text{Co}/\text{Li}<0.975$  might become comparatively are used as a charge of a start material which compounds cobalt acid lithium by this invention. It turned out that mean particle diameter can obtain not less than 5-micrometer cobalt acid lithium, and the totally-solid lithium secondary battery in which a high active material utilization factor is shown by using the cobalt acid lithium obtained by carrying out still in this way as an electrode active material is obtained.

[0106]As mentioned above, according to this invention, it turned out that a totally-solid lithium secondary battery with a high active material utilization factor is obtained.

[0107]Although the example of this invention explained only the thing using the amorphous lithium-ion-conductivity solid electrolyte which becomes considering sulfides including  $\text{Li}_3\text{PO}_4-\text{Li}_2\text{S}-\text{SiS}_2$  glass as a subject as a solid electrolyte, In addition to this as a solid electrolyte, sulfide system noncrystalline solid electrolytes, such as  $\text{Li}_2\text{S}-\text{P}_2\text{S}_5$  and  $\text{LiI}-\text{Li}_2\text{S}-\text{P}_2\text{S}_5$ , Or even when oxide solid electrolytes, such as  $\text{Li}_2\text{O}-\text{B}_2\text{O}_3-\text{SiO}_2$ , and  $\text{Li}_2\text{SO}_4-\text{Li}_2\text{O}-\text{B}_2\text{O}_3$ , are used, the same effect is acquired, and this invention is not limited to what was mentioned as these examples as a solid electrolyte.

[0108]Although the example of this invention explained the totally-solid lithium secondary battery which used titanium disulfide, graphite, cobalt acid lithium, etc. as an electrode active material, The transition metal chalcogenide of others as an electrode active material, such as molybdenum disulfide and niobium selenide, Transition metal oxides, such as manganic acid lithium ( $\text{LiMnO}_2, \text{LiMn}_2\text{O}_4$ ), Or also when the metal which lithium, such as indium powder, an aluminium powder, and aluminium-lithium alloy powder, diffuses in solid phase is used as an electrode active material, the same effect is acquired, and this invention is not limited to what was mentioned as these examples as an electrode active material.

[0109]In order to search for the capacity factor of an electrode active material simple, used active materials, such as titanium disulfide and graphite, as positive active material, and constituted the totally-solid lithium secondary battery from an example of this invention by using a negative electrode as metal lithium foil, but. When a totally-solid lithium secondary battery is constituted using the negative electrode active material of others, such as an aluminium-lithium alloy and an indium lithium alloy, When it combined with the substance in which electropositive potential is shown and the material of a statement is furthermore used for these examples as negative electrode active material as positive active material, For example, even when cobalt acid lithium performs as an anode and it carries out in the combination of graphite or titanium disulfide as a negative electrode, the same effect is acquired and this invention is not limited to the totally-solid lithium secondary battery which used the electrode quoted in these examples for the anode.

[0110]The mean particle diameter of the electrode active material in the claim of this invention and a solid

electrolyte shows the mean particle diameter at the time of mixing these. By on the other hand, the phenomenon of it becoming impossible for grain growth to arise, when these materials are fabricated and a cell is constituted, or to distinguish a grain boundary by carrying out pressing of the amorphous materials etc. By phenomena, like a thing which shows big mean particle diameter, or the minuteness making of an electrode active material arises by repetition of charge and discharge conversely. It cannot be overemphasized that an effect with the same said of what became the outside of the range of the mean particle diameter which changed after both mean particle diameter mixing that small mean particle diameter is shown etc., and was indicated to the generic claim of this invention is acquired.

[0111]

[Effect of the Invention]As explained above, according to this invention, in the composition of a totally-solid lithium secondary battery, mean particle diameter as active material powder 0.1-50 micrometers, The totally-solid lithium secondary battery with a high active material utilization factor was able to be obtained by mixing these powder at a rate of 3.0:7.0 to 9.5:0.5 by a weight ratio, and forming an electrode using the thing whose mean particle diameter is 0.1-50 micrometers as solid electrolyte powder.

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[Translation done.]

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TECHNICAL FIELD

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[Industrial Application]This invention relates to the totally-solid lithium secondary battery which used the lithium-ion-conductivity solid electrolyte as an electrolyte.

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PRIOR ART

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[Description of the Prior Art]In recent years, while a miniaturization and weight saving of portable devices, such as a camcorder/movie and a cellular phone, progress, high-energy-density-ization is desired to the cell as the power supply. Since especially a lithium cell is a substance with an atomic weight with small lithium in which ionization energy is big, research is done briskly [ every direction ] as a cell which can obtain high energy density.

[0003]In the lithium secondary battery used for these uses on the other hand, since the solvent of the organic system is used as an electrolysis solution, it has technical problems, such as a liquid spill and ignition. Therefore, in order to secure the safety of a cell, development of all the solid lithium cells which used the solid electrolyte which comprises a noncombustible solid is desired.

[0004]The method of using the vacuum evaporation techniques, such as a sputtering technique, and thin-film-izing a thin film serves as a subject, and development of all the solid lithium cells is furthered, in order to compensate the lowness of the ion conductivity of the solid electrolyte used. It not only thin-film-izes only a solid electrolyte layer, but by the method of vapor-depositing a thin film, thin film forming also of the electrode material is carried out by vacuum evaporation.

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## EFFECT OF THE INVENTION

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[Effect of the Invention]As explained above, according to this invention, in the composition of a totally-solid lithium secondary battery, mean particle diameter as active material powder 0.1-50 micrometers, The totally-solid lithium secondary battery with a high active material utilization factor was able to be obtained by mixing these powder at a rate of 3.0:7.0 to 9.5:0.5 by a weight ratio, and forming an electrode using the thing whose mean particle diameter is 0.1-50 micrometers as solid electrolyte powder.

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## TECHNICAL PROBLEM

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[Problem(s) to be Solved by the Invention]However, large-area-izing and high-capacity-izing are difficult for all the solid lithium cells by the method of vapor-depositing a thin film, and a charge and discharge current is as small as several 10-200microA cm<sup>2</sup>, and technical problems, like a manufacturing cost also becomes high occur. [0006]When powder molding constitutes an electrode to it, large-area-izing and high capacity-ization are attained and it becomes what also has a low manufacturing cost, but it is necessary to mix solid electrolyte powder to electrode active material powder for the following reason. [0007]In an electrode, electronic transfer is performed during the operation of a cell between the ion and electrode which move in the inside of an electrolyte. Therefore, the electrode of a cell needs to combine ion conductivity and electron conductivity. Generally, when the conductivity of the ion in the inside of an electrode active material and an electrolyte is compared, ion-conductive one in the inside of an electrolyte is high, as a result, electron transfer in the inside of an electrode is performed within an electrode active material or a conducting material, and movement of ion is performed mainly within an electrolyte. [0008]That is, in the case of the cell using a liquid electrolyte, the electrode created by carrying out application-of-pressure molding of the powdered active material is immersed in an electrolyte, and the electrolyte which permeated in the hole of this powder compact serves as a place of the ion conduction within an electrode. [0009]On the other hand, since an electrolyte does not permeate in the hole in an electrode in the case of the electrode using the solid electrolyte as an electrolyte, in order to make high ion conductivity in the inside of an electrode, it is necessary [ it ] in an electrode to mix a solid electrolyte. However, since electron transfer is performed, active material particles need to be connected electronically, and when the amount of solid electrolytes in an electrode is superfluous, there is a possibility that this connection may be lost. [0010]Thus, in a totally-solid battery, an ion conduction course is spoiled depending on the mixture ratio of the solid electrolyte and active material in an electrode, or an electronic conduction course is checked. For this reason, it had a technical problem which the impedance of an electrode becomes high, and the charge and discharge in a high current become difficult, and becomes what has a low active material utilization factor. [0011]When the electrolyte was mixed in the electrode, since the active material content in an electrode will become small, it had a technical problem used as what has the low capacity of a cell. [0012]This invention solves the above technical problem and an object of this invention is to provide the totally-solid lithium secondary battery with a high active material utilization factor using the electrode by powder molding method.

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MEANS

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[Means for Solving the Problem]As an electrode of a totally-solid lithium secondary battery, a mixture which blends active material powder whose mean particle diameter is 0.1-50 micrometers, and solid electrolyte powder whose mean particle diameter is 0.1-50 micrometers by a weight ratio 3.0:7.0 to 9.5:0.5 is used. An amorphous lithium-ion-conductivity solid electrolyte which becomes considering a sulfide as a subject is used as solid electrolyte powder.

[0014]At least one electrode is a thing containing an amorphous lithium-ion-conductivity solid electrolyte which becomes considering cobalt acid lithium and a sulfide as a subject, In a totally-solid lithium secondary battery which is an amorphous lithium-ion-conductivity solid electrolyte which becomes considering a sulfide as a subject, a solid electrolyte layer uses that whose mean particle diameter of cobalt acid lithium is 5-50 micrometers. That whose mean particle diameter is 0.1 micrometer - 50 micrometers is used as a solid electrolyte contained in an electrode. A ratio of cobalt acid lithium contained in an electrode to a solid electrolyte is set to 4.0:6.0 to 9.5:0.5 by a weight ratio.

[0015]Cobalt acid lithium is compounded considering a cobalt oxide and a lithium compound as a charge of a start material, and sets preferably to  $\text{Co/Li} < 0.975$  the mixture ratio of a cobalt oxide and a lithium compound which are starting materials by a weight ratio at  $\text{Co/Li} < 1.0$  and a pan.  $\text{Co}_3\text{O}_4$  is used as a cobalt oxide.

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OPERATION

[Function]The solid electrolyte powder whose mean particle diameter is 0.1-50 micrometers, and the active material powder whose mean particle diameter is 0.1-50 micrometers are used, By carrying out pressing of the mixture which blends these powder by a weight ratio 3.0:7.0 to 9.5:0.5, and forming an electrode, Collecting efficiency is raised and it becomes an electrode in which high current charge and discharge are possible at the same time the both sides of the ion conduction course in an electrode and an electronic conduction course can secure and it raises the capacity factor of the active material in an electrode.

[0017]It is required to use the solid electrolyte in which ionic conductivity high in order to improve the ion conductivity within an electrode is shown as a solid electrolyte used for the electrode of such a totally-solid lithium secondary battery. For this reason, especially the thing for which the amorphous lithium-ion-conductivity solid electrolyte which becomes considering the sulfide in which high lithium ion conductivity is shown as a subject is used as solid electrolyte powder is preferred.

[0018]In an electronic-lithium ion mixing conductor, the totally-solid lithium secondary battery which has an energy density possible [ the operation by a high current ] and high can consist of using the cobalt acid lithium in which high ion conductivity and \*\*\*\* electrode potential are shown as an electrode active material. For this reason, especially the thing for which the electrode containing the amorphous lithium-ion-conductivity solid electrolyte which becomes considering cobalt acid lithium and a sulfide as a subject at least is used as an electrode of a totally-solid lithium secondary battery is preferred.

[0019]It is preferred to raise an active material utilization factor using what has a grain boundary few as cobalt acid lithium used as the hindrance of lithium ion conduction. Therefore, when an electrode is constituted by the application-of-pressure molding method, it is preferred to use [ rather than ] what has big particle diameter using the cobalt acid lithium with small particle diameter in which many grain boundaries will exist, and it is preferred that mean particle diameter uses what is 5-50 micrometers as said cobalt acid lithium.

[0020]In the electrode containing the above-mentioned cobalt acid lithium and an amorphous lithium-ion-conductivity solid electrolyte, Collecting efficiency is raised and it becomes an electrode in which high current charge and discharge are possible at the same time the both sides of the ion conduction course in an electrode and an electronic conduction course can secure because the mean particle diameter of the solid electrolyte contained in an electrode shall be 0.1-50 micrometers, and it raises the capacity factor of the active material in an electrode.

[0021]The both sides of the ion conduction course in an electrode and an electronic conduction course are securable by blending cobalt acid lithium and the solid electrolyte which are contained in an electrode in 4.0:6.0 to 9.5:0.5 by a weight ratio. However, in the range with high content of cobalt acid lithium, the active material content in an electrode is high, Since it becomes what has high capacity density, as a ratio of the cobalt acid lithium contained in an electrode to a solid electrolyte, the range of 6.0:4.0 to 9.5:0.5 is especially used preferably by a weight ratio among the above-mentioned mixture ratio.

[0022]Although cobalt acid lithium is compounded considering a cobalt oxide and a lithium compound as a charge of a start material, the particle diameter of the cobalt acid lithium obtained with the mixture ratio at the time of composition changes. The thing using the starting material in which the mixture ratio of a cobalt oxide and a lithium compound turns into a ratio of Co/Li<1.0 since only what has mean particle diameter comparatively small in Co/Li>=1.0 is obtained is used preferably. Since cobalt acid lithium with a particle diameter of not less than 5 micrometers can be easily obtained by furthermore being referred to as Co/Li<0.975, as the mixture ratio of the lithium compound and cobalt oxide which are charges of a start material, the range of Co/Li<0.975 is used especially preferably.

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[0023] Cobalt acid lithium has a crystal structure similar to the cobalt oxide expressed with  $\text{Co}_3\text{O}_4$ , and the particle size of cobalt acid lithium reflects the particle size of  $\text{Co}_3\text{O}_4$  of a starting material well. For this reason, since the particle diameter of the cobalt acid lithium compounded by choosing the particle diameter of  $\text{Co}_3\text{O}_4$  is easily controllable, as a cobalt oxide of a starting material,  $\text{Co}_3\text{O}_4$  is used especially preferably.

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[Translation done.]

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- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.\*\*\*\* shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

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EXAMPLE

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[Example]Hereafter, although this invention was explained in detail using the example, all operations in these examples were performed all over the dry box which filled inactive gas.

[0025](Example 1) Details are shown below about the totally-solid lithium secondary battery used  $\text{Li}_3\text{PO}_4\text{-Li}_2\text{S-SiS}_2$  glass as a solid electrolyte, used titanium disulfide ( $\text{TiS}_2$ ) as positive active material, and using metal lithium foil as a negative electrode.

[0026]First, titanium disulfide is ground so that mean particle diameter may be set to 0.1 micrometer. Subsequently,  $0.01\text{Li}_3\text{PO}_4\text{-}0.63\text{Li}_2\text{S-}0.36\text{SiS}_2$  glass is ground, and it classifies so that mean particle diameter may be set to 0.1, 25 and 50, and 75 or 100 micrometers. Weighing of disulfide titanium powder and each  $0.01\text{Li}_3\text{PO}_4\text{-}0.63\text{Li}_2\text{S-}0.36\text{SiS}_2$  glass powder which classified is carried out so that it may be set to 1:9-10:0 by a weight ratio, it is mixed enough, and it is considered as anode powder. Weighing of the quantity which contains the titanium disulfide of fixed theoretical capacity for this anode powder was carried out, pressing was carried out to 10 mmphi, and it was considered as the anode.

[0027]Pressing of the  $0.01\text{Li}_3\text{PO}_4\text{-}0.63\text{Li}_2\text{S-}0.36\text{SiS}_2$  glass powder is carried out. It was considered as the solid electrolyte layer with 0.5 mm [ in thickness ], and a diameter [ phi ] of 10 mm, after facing across and welding this solid electrolyte layer by pressure with the metal lithium foil which is the above-mentioned anode and a negative electrode, it inserted in the cell case, and it was considered as the totally-solid lithium secondary battery.

[0028]This totally-solid lithium secondary battery is discharged to 1.8V according to the constant current of 500microA, and the result of having investigated the titanium disulfide capacity factor which is positive active material is shown in drawing 1.

[0029]The result at the time of using that whose mean particle diameter of 1, 2, 3, 4, 5, and \*\*\*\*\*  $0.01\text{Li}_3\text{PO}_4\text{-}0.63\text{Li}_2\text{S-}0.36\text{SiS}_2$  glass powder is 0.1 micrometer, 25 micrometers, 50 micrometers, 75 micrometers, and 100 micrometers is shown among a figure.

[0030]When the mean particle diameter of titanium disulfide is 0.1 micrometer from this result, When the mean particle diameter of  $01\text{Li}_3\text{PO}_4\text{-}0.63\text{Li}_2\text{S-}0.36\text{SiS}_2$  glass powder is 50 micrometers or less, 0. Titanium disulfide and  $0.01\text{Li}_3\text{PO}_4\text{-}0.63\text{Li}_2\text{S-}0.36\text{SiS}_2$  glass. The powdered rate showed the high capacity factor in 3.0:7.0 to 7.0:3.0 by the weight ratio, and the capacity factor of 78% was acquired at the maximum.

[0031](Example 2) Except the mean particle diameter of titanium disulfide having been 25 micrometers, the same totally-solid lithium secondary battery as Example 1 was constituted, and the same examination was done.

[0032]The result is shown in drawing 2. 6, 7, 8, 9, and 10 show among a figure the result at the time of using that whose mean particle diameter of  $0.01\text{Li}_3\text{PO}_4\text{-}0.63\text{Li}_2\text{S-}0.36\text{SiS}_2$  glass powder is 0.1 micrometer, 25 micrometers, 50 micrometers, 75 micrometers, and 100 micrometers respectively.

[0033]When the mean particle diameter of titanium disulfide is 25 micrometers from this result, 0. When the mean particle diameter of  $01\text{Li}_3\text{PO}_4\text{-}0.63\text{Li}_2\text{S-}0.36\text{SiS}_2$  glass powder is 50 micrometers or less, the rate of titanium disulfide and  $0.01\text{Li}_3\text{PO}_4\text{-}0.63\text{Li}_2\text{S-}0.36\text{SiS}_2$  glass powder. The weight ratio showed the high capacity factor in 3.0:7.0 to 7.0:3.0, and the capacity factor of 76% was acquired at the maximum.

[0034](Example 3) Except the mean particle diameter of titanium disulfide having been 50 micrometers, the same totally-solid lithium secondary battery as Example 1 was constituted, and the same examination was done.

[0035]The result is shown in drawing 3. 11, 12, 13, 14, and 15 show among a figure the result at the time of using

that whose mean particle diameter of  $0.01\text{Li}_3\text{PO}_4-0.63\text{Li}_2\text{S}-0.36\text{SiS}_2$  glass powder is 0.1 micrometer, 25 micrometers, 50 micrometers, 75 micrometers, and 100 micrometers respectively.

[0036]When the mean particle diameter of titanium disulfide is 50 micrometers from this result, 0. When the mean particle diameter of  $0.01\text{Li}_3\text{PO}_4-0.63\text{Li}_2\text{S}-0.36\text{SiS}_2$  glass powder is 50 micrometers or less, the rate of titanium disulfide and  $0.01\text{Li}_3\text{PO}_4-0.63\text{Li}_2\text{S}-0.36\text{SiS}_2$  glass powder. The weight ratio showed the high capacity factor in 3.0:7.0 to 7.0:3.0, and the capacity factor of 75% was acquired at the maximum.

[0037](Comparative example 1) Except the mean particle diameter of titanium disulfide having been 75 micrometers, the same totally-solid lithium secondary battery as Example 1 was constituted, and the same examination was done.

[0038]The result is shown in drawing 4. 16, 17, 18, 19, and 20 show among a figure the result at the time of using that whose mean particle diameter of  $0.01\text{Li}_3\text{PO}_4-0.63\text{Li}_2\text{S}-0.36\text{SiS}_2$  glass powder is 0.1 micrometer, 25 micrometers, 50 micrometers, 75 micrometers, and 100 micrometers respectively.

[0039]When the mean particle diameter of titanium disulfide is 75 micrometers from this result, The rate of titanium disulfide and  $0.01\text{Li}_3\text{PO}_4-0.63\text{Li}_2\text{S}-0.36\text{SiS}_2$  glass powder was only a capacity factor of 45% at the maximum, although the peak of the capacity factor of titanium disulfide was accepted focusing on 5.0:5.0 by the weight ratio.

[0040](Comparative example 2) Except the mean particle diameter of titanium disulfide having been 100 micrometers, the same totally-solid lithium secondary battery as Example 1 was constituted, and the same examination was done.

[0041]The result is shown in drawing 5. 21, 22, 23, 24, and 25 show among a figure the result at the time of using that whose mean particle diameter of  $0.01\text{Li}_3\text{PO}_4-0.63\text{Li}_2\text{S}-0.36\text{SiS}_2$  glass powder is 0.1 micrometer, 25 micrometers, 50 micrometers, 75 micrometers, and 100 micrometers respectively.

[0042]When the mean particle diameter of titanium disulfide is 100 micrometers from this result, The rate of titanium disulfide and  $0.01\text{Li}_3\text{PO}_4-0.63\text{Li}_2\text{S}-0.36\text{SiS}_2$  glass powder was only a capacity factor of 33% at the maximum, although the peak of the capacity factor of titanium disulfide was accepted focusing on 5.0:5.0 by the weight ratio.

[0043]From the above result, the mean particle diameter of the  $0.01\text{Li}_3\text{PO}_4-0.63\text{Li}_2\text{S}-0.36\text{SiS}_2$  glass powder which is a solid electrolyte 0.1-50 micrometers, Using what is 0.1-50 micrometers, by a weight ratio, the mean particle diameter of the disulfide titanium powder which is positive active material blends these powder, and it 3.0:7.0 to 7.0:3.0 mixing and by carrying out pressing and forming an electrode. It turned out that the both sides of the ion conduction course in an electrode and an electronic conduction course can secure, and the capacity factor of the titanium disulfide which is the positive active material in an electrode is raised.

[0044](Example 4) Details are shown below about the totally-solid lithium secondary battery used  $\text{Li}_3\text{PO}_4-\text{Li}_2\text{S}-\text{SiS}_2$  glass as a solid electrolyte, used graphite as positive active material, and using metal lithium foil as a negative electrode.

[0045]First, graphite is ground so that mean particle diameter may be set to 0.1 micrometer. Subsequently,  $0.01\text{Li}_3\text{PO}_4-0.63\text{Li}_2\text{S}-0.36\text{SiS}_2$  glass is ground, and it classifies so that mean particle diameter may be set to 0.1 micrometer, 25 micrometers, 50 micrometers, 75 micrometers, and 100 micrometers. Weighing of graphite and each  $0.01\text{Li}_3\text{PO}_4-0.63\text{Li}_2\text{S}-0.36\text{SiS}_2$  glass powder which classified is carried out so that it may be set to 1:9-10:0 by a weight ratio, it is mixed enough, and it is considered as anode powder. Weighing of the quantity which contains the graphite of fixed theoretical capacity for this anode powder was carried out, pressing was carried out to 10 mmphi, and it was considered as the anode.

[0046]Pressing of the  $0.01\text{Li}_3\text{PO}_4-0.63\text{Li}_2\text{S}-0.36\text{SiS}_2$  glass powder is carried out, It was considered as the solid electrolyte layer with 0.5 mm [ in thickness ], and a diameter [ phi ] of 10 mm, after facing across and welding this solid electrolyte layer by pressure with the metal lithium foil which is the above-mentioned anode and a negative electrode, it inserted in the cell case, and it was considered as the totally-solid lithium secondary battery.

[0047]This totally-solid lithium secondary battery was discharged to 0V according to the constant current of 300microA, and the capacity factor of the graphite which is positive active material was investigated. As a result, when the mean particle diameter of graphite is 0.1 micrometer, 0. When the mean particle diameter of  $0.01\text{Li}_3\text{PO}_4-$

0.63Li<sub>2</sub>S-0.36SiS<sub>2</sub> glass powder is 50 micrometers or less, the rate of titanium disulfide and 0.01Li<sub>3</sub>PO<sub>4</sub>-0.63Li<sub>2</sub>S-0.36SiS<sub>2</sub> glass powder. The weight ratio showed the high capacity factor in 3.0:7.0 to 7.0:3.0, and the capacity factor of 75% was acquired at the maximum.

[0048](Example 5) Except the mean particle diameter of graphite having been 25 micrometers, the same totally-solid lithium secondary battery as Example 4 was constituted, and the same examination was done. As a result, when the mean particle diameter of graphite is 25 micrometers, 0. When the mean particle diameter of 0.01Li<sub>3</sub>PO<sub>4</sub>-0.63Li<sub>2</sub>S-0.36SiS<sub>2</sub> glass powder is 50 micrometers or less, the rate of graphite and 0.01Li<sub>3</sub>PO<sub>4</sub>-0.63Li<sub>2</sub>S-0.36SiS<sub>2</sub> glass powder. The weight ratio showed the high capacity factor in 3.0:7.0 to 7.0:3.0, and the capacity factor of 73% was acquired at the maximum.

[0049](Example 6) Except the mean particle diameter of graphite having been 50 micrometers, the same totally-solid lithium secondary battery as Example 4 was constituted, and the same examination was done. As a result, when the mean particle diameter of graphite is 50 micrometers, 0. When the mean particle diameter of 0.01Li<sub>3</sub>PO<sub>4</sub>-0.63Li<sub>2</sub>S-0.36SiS<sub>2</sub> glass powder is 50 micrometers or less, the rate of graphite and 0.01Li<sub>3</sub>PO<sub>4</sub>-0.63Li<sub>2</sub>S-0.36SiS<sub>2</sub> glass powder. The weight ratio showed the high capacity factor in 3.0:7.0 to 7.0:3.0, and the capacity factor of 70% was acquired at the maximum.

[0050](Comparative example 3) Except the mean particle diameter of graphite having been 75 micrometers, the same totally-solid lithium secondary battery as Example 4 was constituted, and the same examination was done. As a result, when the mean particle diameter of graphite is 75 micrometers, although the peak of the capacity factor of graphite is accepted focusing on 5.0:5.0 by a weight ratio, the rate of graphite and 0.01Li<sub>3</sub>PO<sub>4</sub>-0.63Li<sub>2</sub>S-0.36SiS<sub>2</sub> glass powder, It was only a capacity factor of 25% at the maximum.

[0051](Comparative example 4) Except the mean particle diameter of graphite having been 100 micrometers, the same totally-solid lithium secondary battery as Example 4 was constituted, and the same examination was done. As a result, when the mean particle diameter of graphite is 100 micrometers, although the peak of the capacity factor of graphite is accepted focusing on 5.0:5.0 by a weight ratio, the rate of graphite and 0.01Li<sub>3</sub>PO<sub>4</sub>-0.63Li<sub>2</sub>S-0.36SiS<sub>2</sub> glass powder, It was only a capacity factor of 8% at the maximum.

[0052]From the above result, the mean particle diameter of the 0.01Li<sub>3</sub>PO<sub>4</sub>-0.63Li<sub>2</sub>S-0.36SiS<sub>2</sub> glass powder which is a solid electrolyte 0.1-50 micrometers, Using what is 0.1-50 micrometers, by a weight ratio, the mean particle diameter of the graphite powder which is positive active material blends these powder, and it 3.0:7.0 to 7.0:3.0 mixing and by carrying out pressing and forming an electrode, It turned out that the both sides of the ion conduction course in an electrode and an electronic conduction course can secure, and the capacity factor of the graphite which is the positive active material in an electrode is raised.

[0053](Example 7) It is made to be the same as that of Example 1 except having used the nickel acid lithium expressed with LiNiO<sub>2</sub> as positive active material in this example, Li<sub>3</sub>PO<sub>4</sub>-Li<sub>2</sub>S-SiS<sub>2</sub> glass was used as a solid electrolyte, metal lithium foil was used as a negative electrode, and the totally-solid lithium secondary battery was constituted.

[0054]First, nickel acid lithium was compounded by the following methods. Nickel acid lithium mixed lithium hydroxide (LiOH) with nickel oxide (NiO), and compounded it by calcinating at 1000 \*\* among the atmosphere. This compound nickel acid lithium was ground, and it classified so that mean particle diameter might be set to 1 micrometer, 10 micrometers, 50 micrometers, 75 micrometers, and 100 micrometers.

[0055]The 0.01Li<sub>3</sub>PO<sub>4</sub>-0.63Li<sub>2</sub>S-0.36SiS<sub>2</sub> glass powder obtained by the same method as Example 1 as a solid electrolyte is ground, and it classifies so that mean particle diameter may be set to 1 micrometer. Weighing of nickel acid lithium and 0.01Li<sub>3</sub>PO<sub>4</sub>-0.63Li<sub>2</sub>S-0.36SiS<sub>2</sub> glass powder which were obtained above is carried out so that it may be set to 1:9-10:0 by a weight ratio, they are mixed enough, and it is considered as anode powder. Weighing of the quantity which contains nickel acid lithium of fixed theoretical capacity for this anode powder was carried out, pressing was carried out to 10 mmphi, and it was considered as the anode.

[0056]Pressing of the 0.01Li<sub>3</sub>PO<sub>4</sub>-0.63Li<sub>2</sub>S-0.36SiS<sub>2</sub> glass powder is carried out, It was considered as the solid electrolyte layer with 0.5 mm [ in thickness ], and a diameter [ phi ] of 10 mm, after facing across and welding this solid electrolyte layer by pressure with the metal lithium foil which is the above-mentioned anode and a negative electrode, it inserted in the cell case, and the totally-solid lithium secondary battery was constituted. As negative

electrode active material, 100-micrometer-thick metal lithium foil was used.

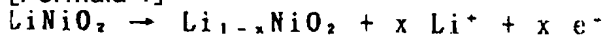
[0057] Thus, the obtained totally-solid lithium secondary battery was charged by the constant current of 100microA, and charging capacity until terminal voltage shows 4.3V was measured.

[0058] The relation between nickel acid lithium in an anode, the rate of  $0.01\text{Li}_3\text{PO}_4-0.63\text{Li}_2\text{S}-0.36\text{SiS}_2$  glass powder, and charging capacity is shown in drawing 6. However, charging capacity is converted into the move electron number (\*\* 1) (inner x value) to nickel acid lithium, and a vertical axis shows it.

[0059] 26, 27, 28, 29, and 30 show among a figure the result at the time of using that whose mean particle diameter of nickel acid lithium is 1 micrometer, 10 micrometers, 50 micrometers, 75 micrometers, and 100 micrometers respectively.

[0060]

[Formula 1]



[0061] From this result, when the mean particle diameter of  $0.01\text{Li}_3\text{PO}_4-0.63\text{Li}_2\text{S}-0.36\text{SiS}_2$  glass powder is 1 micrometer, When the mean particle diameter of nickel acid lithium is 50 micrometers or less, the rate of nickel acid lithium and  $0.01\text{Li}_3\text{PO}_4-0.63\text{Li}_2\text{S}-0.36\text{SiS}_2$  glass powder shows high charging capacity in 4.0:6.0 to 9.5:0.5 by a weight ratio, It turned out that a high active material utilization factor can be obtained.

[0062] As mentioned above, according to this invention, it turned out that the totally-solid lithium secondary battery in which a high active material utilization factor is shown is obtained.

[0063] (Example 8) It is made to be the same as that of Example 1 except having used the cobalt-acid-lithium powder expressed with  $\text{LiCoO}_2$  as an electrode active material in this example,  $\text{Li}_3\text{PO}_4-\text{Li}_2\text{S}-\text{SiS}_2$  glass was used as a solid electrolyte, metal lithium foil was used as a negative electrode, and the totally-solid lithium secondary battery was constituted.

[0064] First, cobalt acid lithium ( $\text{LiCoO}_2$ ) was compounded by the following methods. Cobalt oxide ( $\text{Co}_3\text{O}_4$ ) and lithium carbonate ( $\text{Li}_2\text{CO}_3$ ) were compounded weighing and by mixing and calcinating at 900 \*\* among the atmosphere so that it might become a ratio of  $\text{Co}/\text{Li}=0.96$ . Thus, it was 8 micrometers when the mean particle diameter of the obtained cobalt acid lithium was measured.

[0065] The  $0.01\text{Li}_3\text{PO}_4-0.63\text{Li}_2\text{S}-0.36\text{SiS}_2$  glass powder obtained by the same method as Example 1 as a solid electrolyte is ground, and it classifies so that mean particle diameter may be set to 0.1 micrometer, 1 micrometer, 10 micrometers, 50 micrometers, and 100 micrometers. Weighing of the cobalt acid lithium obtained above and each  $0.01\text{Li}_3\text{PO}_4-0.63\text{Li}_2\text{S}-0.36\text{SiS}_2$  glass powder which classified is carried out so that it may be set to 1:9-10:0 by a weight ratio, it is mixed enough, and it is considered as anode powder. Weighing of the quantity which contains cobalt acid lithium of fixed theoretical capacity for this anode powder was carried out, pressing was carried out to 10 mmphi, and it was considered as the anode.

[0066] Pressing of the  $0.01\text{Li}_3\text{PO}_4-0.63\text{Li}_2\text{S}-0.36\text{SiS}_2$  glass powder is carried out, It was considered as the solid electrolyte layer with 0.5 mm [ in thickness ], and a diameter [ phi ] of 10 mm, after facing across and welding this solid electrolyte layer by pressure with the metal lithium foil which is the above-mentioned anode and a negative electrode, it inserted in the cell case, and the totally-solid lithium secondary battery was constituted. As negative electrode active material, 100-micrometer-thick metal lithium foil was used.

[0067] Thus, the obtained totally-solid lithium secondary battery was charged by the constant current of 200microA, and charging capacity until terminal voltage shows 4.5V was measured.

[0068] The relation between cobalt acid lithium in an anode, the rate of  $0.01\text{Li}_3\text{PO}_4-0.63\text{Li}_2\text{S}-0.36\text{SiS}_2$  glass powder, and charging capacity is shown in drawing 7. However, charging capacity is converted into the move electron number (\*\* 2) (inner x value) to cobalt acid lithium, and a vertical axis shows it.

[0069]

[Formula 2]



[0070] The capacity density of per anode 1g is calculated from the charging capacity produced by doing in this way, The relation between cobalt acid lithium in an anode, the rate of  $0.01\text{Li}_3\text{PO}_4-0.63\text{Li}_2\text{S}-0.36\text{SiS}_2$  glass powder, and the capacity density of per anode 1g is shown in drawing 8.

[0071]The inside [ 36, 37, 38, 39, and 40 ] 31, 32, 33, 34, and 35 of drawing 7 and drawing 8, The result of having used that whose mean particle diameter of  $0.01\text{Li}_3\text{PO}_4-0.63\text{Li}_2\text{S}-0.36\text{SiS}_2$  glass powder is 0.1 micrometer, 1 micrometer, 10 micrometers, 50 micrometers, and 100 micrometers respectively is shown.

[0072]When the particle diameter of cobalt acid lithium is 8 micrometers from the result shown in drawing 7, When the mean particle diameter of  $0.01\text{Li}_3\text{PO}_4-0.63\text{Li}_2\text{S}-0.36\text{SiS}_2$  glass powder is 0.1–50 micrometers, 0. Cobalt acid lithium and  $0.01\text{Li}_3\text{PO}_4-0.63\text{Li}_2\text{S}-0.36\text{SiS}_2$  glass. It turned out that a powdered rate shows high charging capacity in 4.0:6.0 to 9.5:0.5 by a weight ratio, and can obtain a high active material utilization factor. From the result shown in drawing 8. It turned out that the totally-solid lithium secondary battery which the rate of cobalt acid lithium and  $0.01\text{Li}_3\text{PO}_4-0.63\text{Li}_2\text{S}-0.36\text{SiS}_2$  glass powder shows high capacity density especially in 6.0:4.0 to 9.5:0.5 by a weight ratio is obtained.

[0073]As mentioned above, according to this invention, it turned out that the totally-solid lithium secondary battery in which a high active material utilization factor is shown, and high capacity density is shown is obtained.

[0074](Example 9) In this example, it replaces with  $0.01\text{Li}_3\text{PO}_4-0.63\text{Li}_2\text{S}-0.36\text{SiS}_2$  as an electrolyte, 0. Except having used the lithium-ion-conductivity noncrystalline solid electrolyte expressed with  $60\text{Li}_2\text{S}-0.40\text{SiS}_2$ , the totally-solid lithium secondary battery was constituted from the same method as Example 8, and the characteristic was evaluated.

[0075]As a result, the relation of the active material utilization factor and capacity density to the mixture ratio of the active material and solid electrolyte in an electrode was the same as that of Example 8 almost.

[0076]As mentioned above, according to this invention, it turned out that the totally-solid lithium secondary battery in which a high active material utilization factor is shown, and high capacity density is shown is obtained.

[0077](Example 10) In this example, it replaces with  $0.01\text{Li}_3\text{PO}_4-0.63\text{Li}_2\text{S}-0.36\text{SiS}_2$  as an electrolyte, 0. Except having used the lithium-ion-conductivity noncrystalline solid electrolyte expressed with  $04\text{Li}_4\text{SiO}_4-0.58\text{Li}_2\text{S}-0.38\text{SiS}_2$ , all the solid lithium cells were constituted from the same method as Example 8, and the characteristic was evaluated.

[0078]As a result, the relation of the active material utilization factor and capacity density to the mixture ratio of the active material and solid electrolyte in an electrode was the same as that of Example 8 almost.

[0079]As mentioned above, according to this invention, it turned out that the totally-solid lithium secondary battery in which a high active material utilization factor is shown, and high capacity density is shown is obtained.

[0080](Example 11) In this example, it replaces with  $0.01\text{Li}_3\text{PO}_4-0.63\text{Li}_2\text{S}-0.36\text{SiS}_2$  as an electrolyte, 0. Except having used the lithium-ion-conductivity noncrystalline solid electrolyte expressed with  $02\text{Li}_2\text{O}-0.59\text{Li}_2\text{S}-0.39\text{SiS}_2$ , the totally-solid lithium secondary battery was constituted from the same method as Example 8, and the characteristic was evaluated.

[0081]As a result, the relation of the active material utilization factor and capacity density to the mixture ratio of the active material and solid electrolyte in an electrode was the same as that of Example 8 almost.

[0082]As mentioned above, according to this invention, it turned out that the totally-solid lithium secondary battery in which a high active material utilization factor is shown, and high capacity density is shown is obtained.

[0083](Example 12) In this example, it replaces with  $0.01\text{Li}_3\text{PO}_4-0.63\text{Li}_2\text{S}-0.36\text{SiS}_2$  as an electrolyte, 0. Except having used the lithium-ion-conductivity noncrystalline solid electrolyte expressed with  $60\text{Li}_2\text{S}-0.35\text{SiS}_2-0.05\text{P}_2\text{S}_5$ , the totally-solid lithium secondary battery was constituted from the same method as Example 8, and the characteristic was evaluated.

[0084]As a result, the relation of the active material utilization factor and capacity density to the mixture ratio of the active material and solid electrolyte in an electrode was the same as that of Example 8 almost.

[0085]As mentioned above, according to this invention, it turned out that the totally-solid lithium secondary battery in which a high active material utilization factor is shown, and high capacity density is shown is obtained.

[0086](Example 13) In order to investigate a relation with the mixture ratio of the active material and solid electrolyte in the active material powder grain size at the time of using cobalt acid lithium as an electrode active material, and an electrode in this example, The totally-solid lithium secondary battery was constituted like Example 8 using the cobalt-acid-lithium powder of various particle diameter as an electrode active material, and the characteristic was evaluated.



[0087]It compounded by calcinating cobalt oxide and lithium carbonate at 900 \*\* among the atmosphere as cobalt acid lithium (LiCoO<sub>2</sub>), using weighing and the mixed thing as a starting material so that it may become a ratio of Co/Li=0.92. Thus, grinding classification of the obtained cobalt acid lithium is carried out, and it classifies so that mean particle diameter may be set to 0.1 micrometer, 1 micrometer, 5 micrometers, 10 micrometers, 50 micrometers, and 100 micrometers.

[0088]As a solid electrolyte, the 0.01Li<sub>3</sub>PO<sub>4</sub>-0.63Li<sub>2</sub>S-0.36SiS<sub>2</sub> glass powder obtained by the same method as Example 1 was ground, and what was classified so that mean particle diameter might be set to 1 micrometer was used.

[0089]The totally-solid lithium secondary battery obtained by creating like Example 8 using these was charged by the same method as Example 8, and the charging capacity was measured.

[0090]The relation between nickel acid lithium in the anode of cobalt acid lithium of each mean particle diameter, the rate of 0.01Li<sub>3</sub>PO<sub>4</sub>-0.63Li<sub>2</sub>S-0.36SiS<sub>2</sub> glass powder, and charging capacity is shown in drawing 9.

[0091]41, 42, 43, 44, 45, and 46 show among a figure the result at the time of using that whose mean particle diameter of cobalt acid lithium is 0.1 micrometer, 1 micrometer, 5 micrometers, 10 micrometers, 50 micrometers, and 100 micrometers respectively.

[0092]From this result. When the mean particle diameter of cobalt acid lithium is 5-50 micrometers, the rate of cobalt acid lithium and 0.01Li<sub>3</sub>PO<sub>4</sub>-0.63Li<sub>2</sub>S-0.36SiS<sub>2</sub> glass powder shows high charging capacity in 4.0:6.0 to 9.5:0.5 by a weight ratio, It turned out that a high active material utilization factor can be obtained.

[0093]As mentioned above, according to this invention which sets mean particle diameter of cobalt acid lithium to 5-50 micrometers, it turned out that the totally-solid lithium secondary battery in which a high active material utilization factor is shown is obtained.

[0094](Example 14) In this example, using the cobalt acid lithium which compounded cobalt oxide of the various mixture ratio, and the mixture of lithium carbonate as a starting material as an electrode active material, the totally-solid lithium secondary battery was constituted and the characteristic was evaluated.

[0095]It compounded by calcinating cobalt oxide and lithium carbonate at 900 \*\* among the atmosphere as cobalt acid lithium (LiCoO<sub>2</sub>), using weighing and the mixed thing as a starting material so that it may become a ratio of Co/Li=0.90 - 1.05 as shown in (Table 1).

[0096]Thus, the result of having measured the mean particle diameter of the obtained cobalt acid lithium is shown in (Table 1). Inside "lump" is not powdered and it is shown that massive cobalt acid lithium was obtained (Table 1).

[0097]

[Table 1]

Co/Li	0.90	0.925	0.95	0.975	1.00	1.025	1.05
平均粒径	塊	塊	8	6	4	3	3

[0098]Thus, the totally-solid lithium secondary battery consisted of the following methods using the obtained cobalt acid lithium.

[0099>About the thing of Co/Li=0.90 and 0.925, the obtained sample was ground among the above-mentioned cobalt acid lithium, and what was classified so that mean particle diameter might be set to 8 micrometers was used as an electrode active material. About the thing (Co/Li>0.925) of other presentations, the sample after calcination was used as an electrode active material as it was.

[0100]As a solid electrolyte, the 0.01Li<sub>3</sub>PO<sub>4</sub>-0.63Li<sub>2</sub>S-0.36SiS<sub>2</sub> glass powder with a mean particle diameter of 1 micrometer used in Example 13 is used, Weighing of this 0.01Li<sub>3</sub>PO<sub>4</sub>-0.63Li<sub>2</sub>S-0.36SiS<sub>2</sub> glass powder was carried out so that it might be set to 1:9 by above-mentioned cobalt-acid-lithium powder and weight ratio, it was mixed enough, and it was considered as anode powder. Except having used this positive electrode material, the totally-solid lithium secondary battery was constituted from the same method as Example 8, it charged by the same method as Example 8, and that charging capacity was investigated.

[0101] Thus, cobalt acid lithium in an anode, the rate of  $0.01\text{Li}_3\text{PO}_4-0.63\text{Li}_2\text{S}-0.36\text{SiS}_2$  glass powder, and the relation of charging capacity are shown in drawing 10 about cobalt acid lithium of each obtained mean particle diameter.

[0102] The inside of a figure, and 47, 48, 49, 50, 51, 52 and 53, It is the result of using the cobalt acid lithium which compounded as a starting material what mixed lithium carbonate with cobalt oxide respectively by the ratio of  $\text{Co}/\text{Li}=0.90, 0.925, 0.95, \text{ and } 0.975, 1.00, 1.025 \text{ and } 1.05$ .

[0103] The active material utilization factor in which cobalt acid lithium mixed by the ratio of  $\text{Co}/\text{Li}<1.0$  and the cobalt acid lithium which compounded lithium carbonate as a starting material are more expensive than this result is shown, It turned out that a high active material utilization factor is especially shown by using the starting material mixed by the ratio of  $\text{Co}/\text{Li}<0.975$  furthermore.

[0104] Especially about the thing of  $\text{Co}/\text{Li}=1.00, \text{ and } 1.025 \text{ and } 1.05$ , it turned out to it that only a low active material utilization factor is shown and it is not suitable for the electrode active material of high capacity density in the range in which the content of cobalt acid lithium exceeds 50wt%.

[0105] By as mentioned above, the thing for which  $\text{Co}/\text{Li}<1.0$  and the mixture mixed so that further especially  $\text{Co}/\text{Li}<0.975$  might become comparatively are used as a charge of a start material which compounds cobalt acid lithium by this invention. It turned out that mean particle diameter can obtain not less than 5-micrometer cobalt acid lithium, and the totally-solid lithium secondary battery in which a high active material utilization factor is shown by using the cobalt acid lithium obtained by carrying out still in this way as an electrode active material is obtained.

[0106] As mentioned above, according to this invention, it turned out that a totally-solid lithium secondary battery with a high active material utilization factor is obtained.

[0107] Although the example of this invention explained only the thing using the amorphous lithium-ion-conductivity solid electrolyte which becomes considering sulfides including  $\text{Li}_3\text{PO}_4-\text{Li}_2\text{S}-\text{SiS}_2$  glass as a subject as a solid electrolyte, In addition to this as a solid electrolyte, sulfide system noncrystalline solid electrolytes, such as  $\text{Li}_2\text{S}-\text{P}_2\text{S}_5$  and  $\text{LiI}-\text{Li}_2\text{S}-\text{P}_2\text{S}_5$ , Or even when oxide solid electrolytes, such as  $\text{Li}_2\text{O}-\text{B}_2\text{O}_3-\text{SiO}_2$ , and  $\text{Li}_2\text{SO}_4-\text{Li}_2\text{O}-\text{B}_2\text{O}_3$ , are used, the same effect is acquired, and this invention is not limited to what was mentioned as these examples as a solid electrolyte.

[0108] Although the example of this invention explained the totally-solid lithium secondary battery which used titanium disulfide, graphite, cobalt acid lithium, etc. as an electrode active material, The transition metal chalcogenide of others as an electrode active material, such as molybdenum disulfide and niobium selenide, Transition metal oxides, such as manganic acid lithium ( $\text{LiMnO}_2, \text{LiMn}_2\text{O}_4$ ), Or also when the metal which lithium, such as indium powder, an aluminium powder, and aluminium-lithium alloy powder, diffuses in solid phase is used as an electrode active material, the same effect is acquired, and this invention is not limited to what was mentioned as these examples as an electrode active material.

[0109] In order to search for the capacity factor of an electrode active material simple, used active materials, such as titanium disulfide and graphite, as positive active material, and constituted the totally-solid lithium secondary battery from an example of this invention by using a negative electrode as metal lithium foil, but. When a totally-solid lithium secondary battery is constituted using the negative electrode active material of others, such as an aluminium-lithium alloy and an indium lithium alloy, When it combined with the substance in which electropositive potential is shown and the material of a statement is furthermore used for these examples as negative electrode active material as positive active material, For example, even when cobalt acid lithium performs as an anode and it carries out in the combination of graphite or titanium disulfide as a negative electrode, the same effect is acquired and this invention is not limited to the totally-solid lithium secondary battery which used the electrode quoted in these examples for the anode.

[0110] The mean particle diameter of the electrode active material in the claim of this invention and a solid electrolyte shows the mean particle diameter at the time of mixing these. By on the other hand, the phenomenon of it becoming impossible for grain growth to arise, when these materials are fabricated and a cell is constituted, or to distinguish a grain boundary by carrying out pressing of the amorphous materials etc. By phenomena, like a thing which shows big mean particle diameter, or the minuteness making of an electrode active material arises by repetition of charge and discharge conversely. It cannot be overemphasized that an effect with the same said of what became the outside of the range of the mean particle diameter which changed after both mean particle diameter mixing that small mean particle diameter is shown etc., and was indicated to the generic claim of this

invention is acquired.

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[Translation done.]

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## DESCRIPTION OF DRAWINGS

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### [Brief Description of the Drawings]

[Drawing 1]The figure showing the capacity factor of titanium disulfide and the titanium disulfide to the compounding ratio of  $\text{Li}_3\text{PO}_4\text{-Li}_2\text{S-SiS}_2$  solid electrolyte glass (the 1).

[Drawing 2]The figure showing the capacity factor of titanium disulfide and the titanium disulfide to the compounding ratio of  $\text{Li}_3\text{PO}_4\text{-Li}_2\text{S-SiS}_2$  solid electrolyte glass (the 2).

[Drawing 3]The figure showing the capacity factor of titanium disulfide and the titanium disulfide to the compounding ratio of  $\text{Li}_3\text{PO}_4\text{-Li}_2\text{S-SiS}_2$  solid electrolyte glass (the 3).

[Drawing 4]The figure showing the capacity factor of titanium disulfide and the titanium disulfide to the compounding ratio of  $\text{Li}_3\text{PO}_4\text{-Li}_2\text{S-SiS}_2$  solid electrolyte glass (the 4).

[Drawing 5]The figure showing the capacity factor of titanium disulfide and the titanium disulfide to the compounding ratio of  $\text{Li}_3\text{PO}_4\text{-Li}_2\text{S-SiS}_2$  solid electrolyte glass (the 5).

[Drawing 6]The figure showing the move electron number per [ to the compounding ratio of nickel acid lithium and  $\text{Li}_3\text{PO}_4\text{-Li}_2\text{S-SiS}_2$  solid electrolyte glass ] 1 mol of nickel acid lithium.

[Drawing 7]The figure showing the move electron number per [ to the compounding ratio of cobalt acid lithium and  $\text{Li}_3\text{PO}_4\text{-Li}_2\text{S-SiS}_2$  solid electrolyte glass ] 1 mol of cobalt acid lithium (the 1).

[Drawing 8]The figure showing the charging capacity density of per anode 1g to the compounding ratio of cobalt acid lithium and  $\text{Li}_3\text{PO}_4\text{-Li}_2\text{S-SiS}_2$  solid electrolyte glass.

[Drawing 9]The figure showing the move electron number per [ to the compounding ratio of cobalt acid lithium and  $\text{Li}_3\text{PO}_4\text{-Li}_2\text{S-SiS}_2$  solid electrolyte glass ] 1 mol of cobalt acid lithium (the 2).

[Drawing 10]The figure showing the move electron number per [ to the compounding ratio of cobalt acid lithium and  $\text{Li}_3\text{PO}_4\text{-Li}_2\text{S-SiS}_2$  solid electrolyte glass ] 1 mol of cobalt acid lithium (the 3).

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[Translation done.]

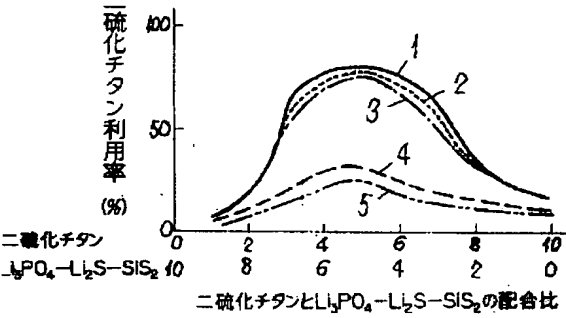
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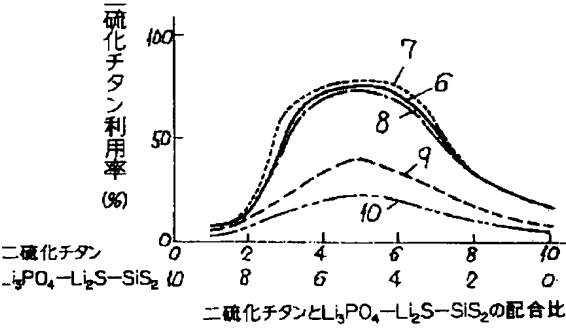
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DRAWINGS

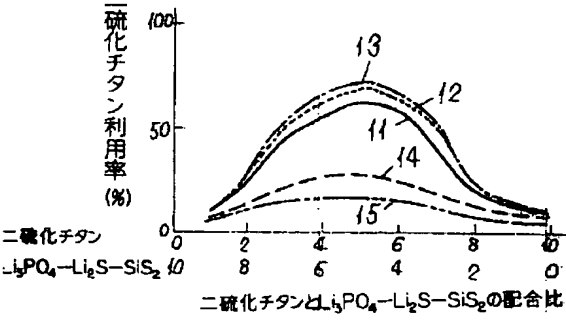
[Drawing 1]



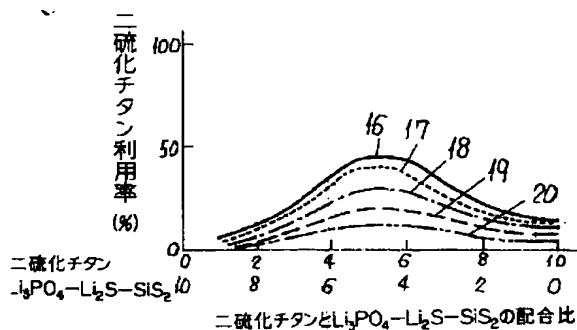
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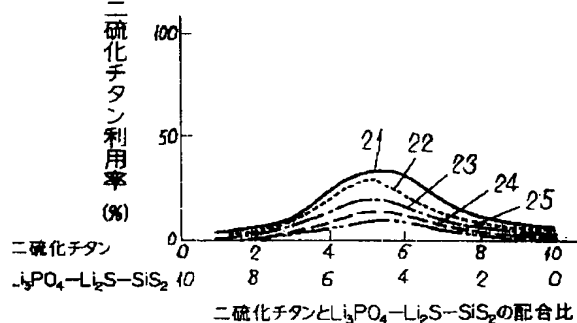
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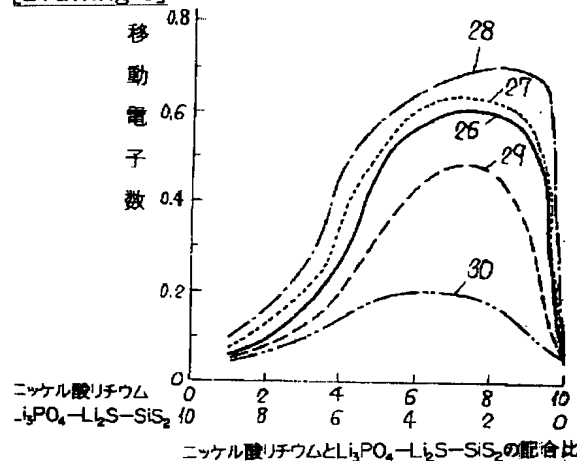
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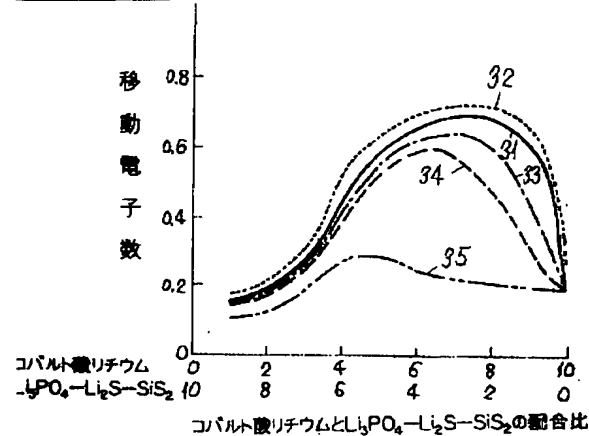
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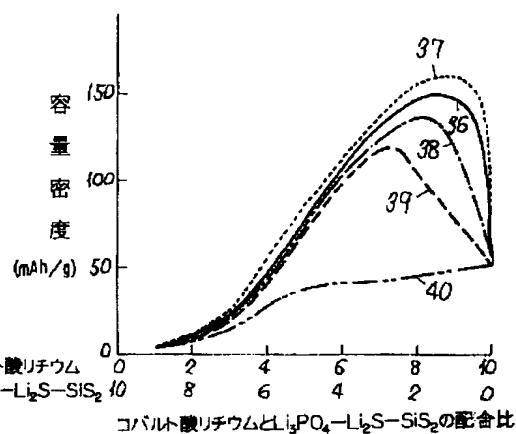
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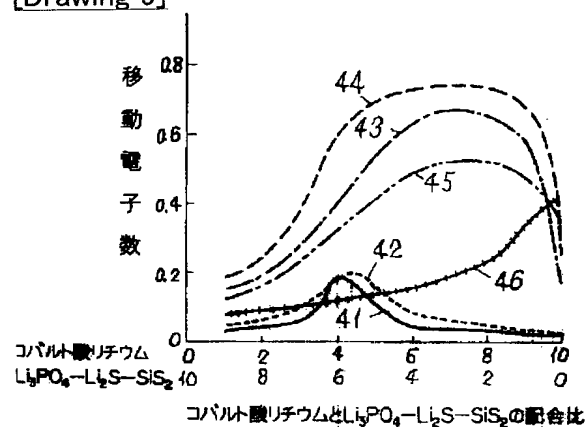
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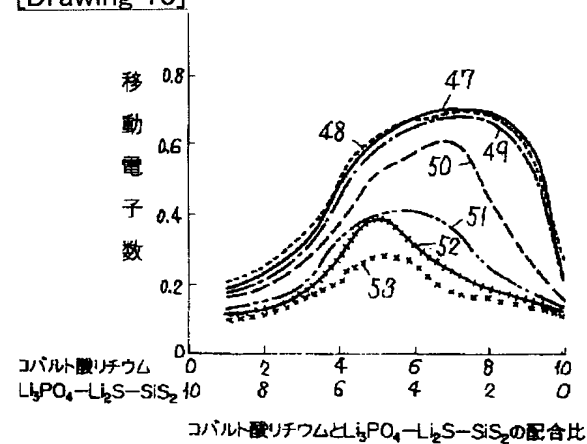
[Drawing 8]



[Drawing 9]



[Drawing 10]



[Translation done.]